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Morphological evolution of ternary $In_xGa_{1-x}As$ nanowires (NWs) grown with Au particle-assisted using vertical chamber MOCVD

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ABSTRACT

The morphology and chemical composition of $In_xGa_{1-x}As$ NWs grown on undoped GaAs (111)B substrate have been investigated using scanning electron microscopy (SEM) and energy dispersive x-ray (EDX), respectively. SEM images show that $In_xGa_{1-x}As$ NWs underwent morphological evolution as temperature changes. By changing the growth temperature, the growth mechanism of NWs was assumed to have changed. Both characterizations results suggested the growth mechanism has strong influence to the evolution of the NWs morphologies and also to the distribution of the chemical composition of NWs.

| $In_xGa_{1-x}As$ NWs | Morphological Evolution | Chemical Composition | Growth mechanism |

1. INTRODUCTION

III-V compound semiconductor nanowires (NWs) have been receiving a lot of attention as base components for the next generation electronic and optoelectronic devices [1-4]. Among them, ternary alloy NWs offer an advantage over elemental or binary NWs in terms of the ability to modify the energy band gap and lattice constant by adjusting the relative composition of the alloy [5]. Furthermore, ternary NWs are required in order to broaden the application range of the NWs on more complicated structures including complex axial as well as radial NWs hetrostructures [3].

$In_xGa_{1-x}As$ NWs is one of the most attractive III-V ternary alloy NWs to be further elaborated due to paramount importance of this material system for application in long wavelength optical transmission and integrated photonics [4,5]. Besides, $In_xGa_{1-x}As$ is considered to be one of the suitable materials for transistor channel due to its low electron effective mass [6,7]. For this application, the NWs needs to be controllable in width and length with dimensions of a few tens of nanometers and several micrometers, respectively. In addition, the well-controlled NWs growth process with appropriate growth parameters must be acquired in order to achieve ternary NWs with good structural, morphology, as well as good chemical composition.

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The most common model to describe particle-assisted NWs has been the vapor liquid solid (VLS) model [5, 8-14], already developed in the 60's [8]. In this model vapor donates the phase of precursors, liquid the phase of particles, and solid the phase of wires. However, it has been reported that the particle could also be in a solid state when growth occurs, and the vapor solid solid (VSS) model has been recommended [15-18]. Those mechanisms depend on growth technique, growth condition as well as material of NWs grown [19]. In particular, III-V NWs can be epitaxially grown by metalorganic chemical vapor deposition (MOCVD) [20]. In the NWs growth process using MOCVD, nanoparticle such as gold as a seed promotes anisotropic wire-like growth by either a vapour-liquid-solid (VLS) or vapor-solid-solid (VSS) mechanism [3, 19]. At growth temperature, the Au nanoparticles on the semiconductor substrate surface form a liquid (for VLS) or solid (for VSS) alloy with the group III species [3]. As the group III species precipitate out at the nanoparticle-semiconductor interface, highly NWs growth occurs, with Au nanoparticle a top each NWs [3, 8-14]. It has been reported that seed (catalytic) growth represents a powerful method for producing 1D nanostructure [19]. The diameter and the length of NWs are mainly determined by the size of the seed and growth time as well as growth conditions, respectively [21]. In this paper, the effect of variation growth temperature to the evolution of the $In_xGa_{1-x}As$ NWs morphology is investigated.

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2. EXPERIMENTAL

The $In_xGa_{1-x}As$ NWs have been grown on undoped GaAs (111)B substrates in vertical chamber MOCVD system. The chamber is set at relatively low pressure (0.1 atm) with hydrogen as carrier gas. $In_xGa_{1-x}As$ NWs were grown using trimethylindium (TMIn), trimethilgallium (TMGa) and arsine (AsH_3) as precursors. Prior to the NWs growth on the substrate surface, the substrate was functionalized by immersing it in 0.1 % poly-L-lisine (PLL) solution for 3 minutes. Then, the substrate was cleaned with de-ionized water and subsequently dried with nitrogen (N_2). It was then treated with 50 % gold colloid solution for 30 seconds. The negatively charged of Au particles are attracted to the positively charged PLL layer thus are immobilized on the substrate surface [1, 2].

The substrate was placed in MOCVD chamber after gold seed particles were deposited on substrate surface. Substrate was initially heated to 600°C under constant partial pressure of AsH_3 gas for 10 minutes, and then cooled to desired growth temperature. Once the growth temperature was achieved, TMIn, TMGa, and AsH_3 were flowed into the chamber and the growth begun. The growth time and V/III ratio were set at 30 minutes and 16.7, respectively. Samples were investigated using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) to investigate the morphology and the chemical composition of the NWs, respectively.

In this growth process, NWs were seeded by 30 nm diameter Au particles. Gold seeded-particles assisted growth of NWs usually grow in the [111] direction which means that when a [111] oriented substrate is used; the NWs grow perpendicular to the substrate [22]. Low growth temperatures between 400 and 475 °C have been chosen for the growth of $In_xGa_{1-x}As$ NWs. These temperatures range is below the pseudobinary eutectic point Au-GaAs (630 °C) [23]. Therefore, the state of Au seed particle is solid or molten - its surface and interface are liquid, while the core of the seed particle is solid [24]. For that reason, $In_xGa_{1-x}As$ NWs have been grown via VSS rather than VLS mechanism.

3. RESULTS & DISCUSSION

Figure 1 shows SEM images of $In_xGa_{1-x}As$ NWs grown for 30 minutes at different growth temperatures. Morphology of NWs looks very different even grown at narrow range of growth temperatures. $In_xGa_{1-x}As$ NWs were grown at 400 °C are perpendicular to the substrate. Even though they not uniform in size, almost all the NWs grown are cylindrical shape without any kinking. Tapering of the NWs starts to occur when the NWs were grown at 425 °C. The NWs grown at this temperature have low NWs density. Small clusters were also observed growing on the substrate. The tapering NWs grew with many big clusters surrounding them were produced when they were grown at 450 °C. Then at 465 °C, the NWs grew in random direction with highly tapering. Once the growth temperature was increased to 475 °C, however, highly tapering NWs grew perpendicularly to the substrate with high NWs density and uniform growth direction.

This phenomenon can be interpreted as due to different mechanism of NWs growth when the growth temperature was changed. The growth mechanism of NWs assisted by Au-seed particles is highly dependable on the growth temperature. It can be seen that at 400 °C, $In_xGa_{1-x}As$ NWs are grow upstraight with relatively cylindrical shape (Fig 1(a)). This phenomenon occurs due to NWs grow through direct impinging mechanism (Fig 2). In this mechanism, atoms from precursors (In, Ga, As) fall directly onto Au seed particle to form an (unstable or stable) alloy, a true eutectic or liquid solution (partially molten state), which serve as a preferential site for the decomposition of the source atoms via absorption (stage 1 of Fig 2(a)), diffusion (stage 2 of Fig 2(a)) and precipitation (stage 3 of Fig 2(a)) [24]. Then locally increase the amount of precursor in the vapor near seed particle compared to elsewhere on the substrate [25]. At a certain point when enough precursor material has been incorporated into the seed particle it will become supersaturated. In this case, saturation of seed particle with the growth precursor or the formation of the proper combination may lead to an induction period before growth [19]. Then, the super saturation leads to precipitation of the semiconductor material at the particle-substrate interface referred to as nucleation (stage 3 Fig 2(a)), then $In_xGa_{1-x}As$ NWs start to grow (Fig 2(b)). By a continuous supply of growth precursors, $In_xGa_{1-x}As$ NWs growth occurs at the particle-wire interface (Fig 2(c)). The growth rate of NWs depends to a large extent on the precursor concentration and the growth temperature [22].

On the other hand, tapering NWs grow with bigger size at the bottom, due to the combination of direct impinging mechanism and diffusion from the substrate surface mechanism (Figure3(b)). In this case, the growth of the NWs were not only due to the direct impinging source atoms onto seed particle, but also from the diffusion of adatoms from substrate surface to the NWs sidewalls towards the seed particle [6, 24]. Increasing the growth temperature give additional energy to source atoms (precursor), therefore precursor atoms that fall onto the substrate surface obtain extra energy to move through substrate surface via diffusion mechanism. Since the seed particle act as the preferential site (lower energy barrier than elsewhere) for the decomposition of the source atoms which lead to nucleation, source atoms from the substrate surface tend to move towards the seed particles and contribute to the growth of the NWs via diffusion mechanism and cause tapering.

At certain growth conditions (high temperature) however, adatom diffusion mechanism from substrate surface could be highly dominant compared to the direct impinging mechanism. Therefore, $In_xGa_{1-x}As$ NWs grown by this mechanism are highly in tapered form whereby the top of the NWs is highly small compared to the base of the NWs. Once the growth temperature is elevated, the rate of atom diffusion increased. Consequently, the diffusion mechanism of source atoms through the substrate is more dominant and contributes to the growth of the NWs. As a result, at certain temperature, the NWs tend to grow solely via diffusion source atoms mechanism. Schematic growth mechanism of $In_xGa_{1-x}As$ NWs is shown in Figure 3(b).

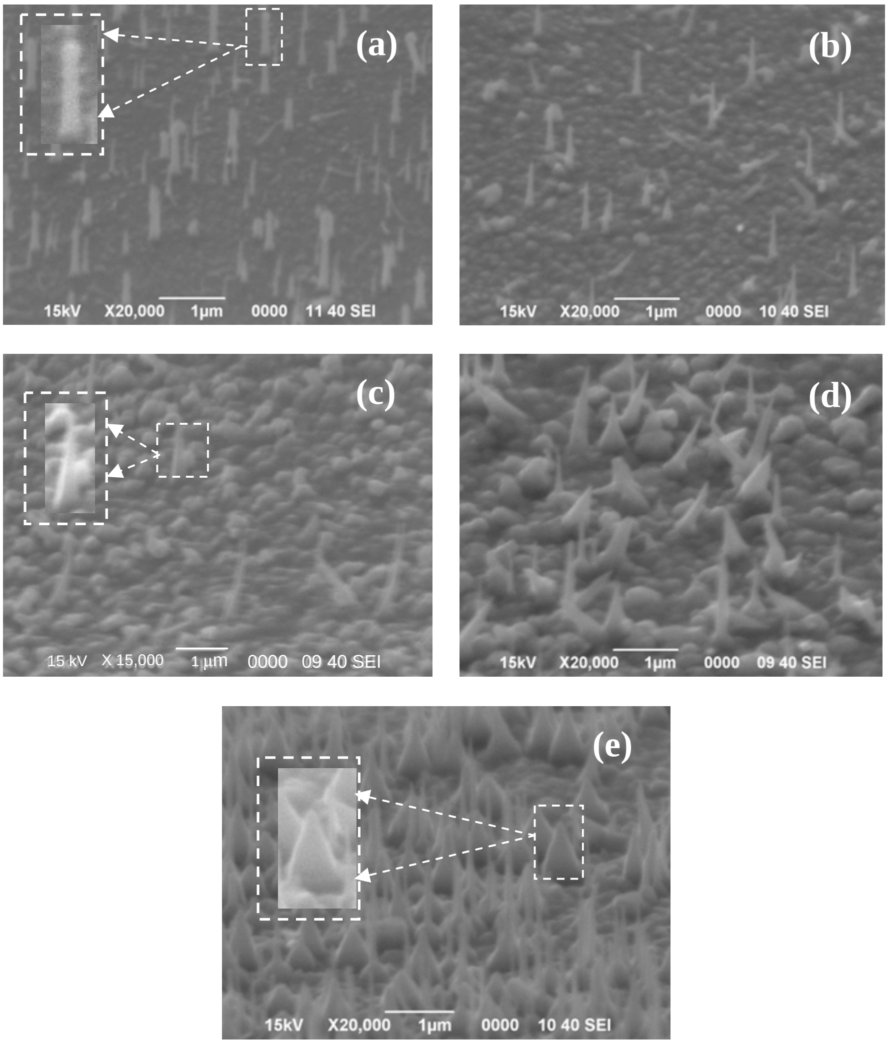

Figure 1: SEM images of $In_xGa_{1-x}As$ NWs seeded by 30 nm diameter Au particles and grown for 30 minutes at (a) 400 °C, (b) 425 °C, (c) 450 °C, (d) 465 °C and (e) 475 °C. Samples were tilted at 45 °. Insets are the enlarged version of selected areas

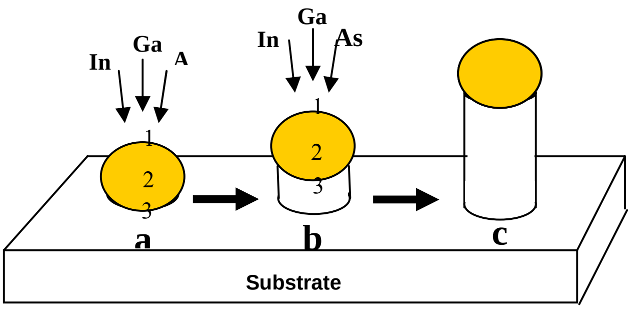

Figure 2: The schematic of direct impinging growth mechanism of $In_xGa_{1-x}As$ NWs. The metal droplet (seed particle) is in solid or partially molten state (liquid solution)

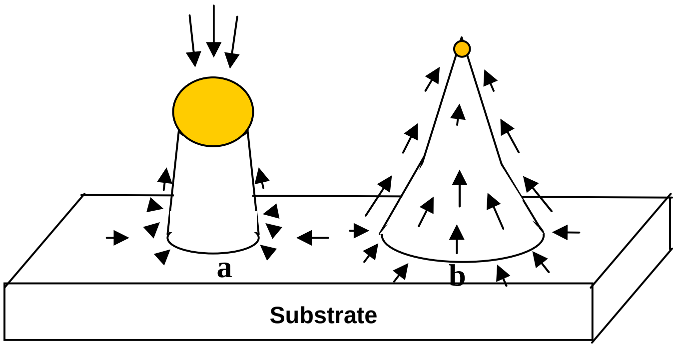

Figure 3: Different growth mechanisms model for the source atoms incorporate into the growth of $In_xGa_{1-x}As$ NWs. The metal droplet (seed particle) is in solid or partially molten state, (a) combination of direct impinging and diffusion source atoms from substrate surface (b) domination of diffusion of source atoms from substrate surface

In the case of $In_xGa_{1-x}As$ NWs growth, the NW grew predominantly via direct impinging mechanism at 400 ^oC then underwent evolution to grow via a different mechanism which is dominated by the adatoms diffusion from the substrate surface when temperature increases above 475 ^oC. Therefore, the growth temperature selection is one of the importance aspects that must be considered for the $In_xGa_{1-x}As$ NWs growth.

Table 1: EDX results of $In_xGa_{1-x}As$ NWs grown at different growth temperature

No	Growth temperature (^{o}C)	Average (In/Ga) ratio		
		Tip	Middle	Bottom
1	400	1.479	1.456	1.473
2	425	1.578	1.623	1.654
3	450	1.171	1.354	1.821
4	465	1.085	1.411	1.895
5	475	2.048	2.439	2.961

EDX analysis was used to investigate the chemical composition of $In_xGa_{1-x}As$ NWs grown at different temperatures from various detection positions; tip, middle and bottom of NWs. From EDX results the ratio of In/Ga compositional at the tip, middle and bottom of the $In_xGa_{1-x}As$ NWs was not uniform as shown in Table 1. Surprisingly, Au was not detected from various detection positions, even on the tip of the NWs. This was most likely due to the amount of Au was very small compared to the elements of the NWs. Based on the EDX results, it can be identified that NWs grown at 400 ^oC via direct impinging mechanism has relatively uniform chemical composition. NWs were grown at temperature of 475 ^oC that grew via the adatoms diffusion mechanism from the substrate surface has highest deviation in composition along the NWs. The EDX results give evident that the growth mechanisms of NWs were highly contributed to the morphological formation as well as in the chemical composition distribution of the NWs. Consequently, to produce $In_xGa_{1-x}As$ NWs with cylindrical shape, uniform size and chemical composition, NWs should be grown via direct impinging mechanism at the appropriate temperature.

4. CONCLUSION

Morphological evolution of $In_xGa_{1-x}As$ NWs from cylindrical to tapering shape is caused by changes in growth mechanism. The growth mechanism itself is dependable on the growth temperature. Cylindrical $In_xGa_{1-x}As$ NWs grew perpendicular to the substrate at 400 ^oC but then changed dramatically to tapering at 475^{o}C. By changing the growth temperature, the growth mechanism of NWs may change. EDX result shows that the cylindrical NWs have more uniform chemical composition compared to the tapering shape. Both characterizations results show that the growth mechanisms of NWs were highly contributed to the morphological formation as well as the chemical composition distribution of the NWs. Further study should be done in order to produce $In_xGa_{1-x}As$ NWs that grow perpendicular to the substrate surface with more controllable morphology, size (diameter and length) and NWs density.

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